SINGLE CRYSTAL ESR STUDY OF COPPER(II)-BIS (1,1-DICYANOETHYLENE-2,2-DITHIOLATE)

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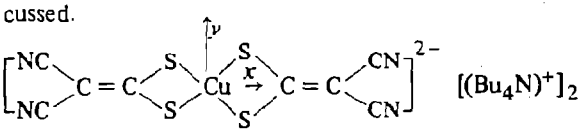
A single crystal ESR study of $[Cu(i\text{-}MNT)_2]$ $(Bu_4N)_2$ diluted in the corresponding nickel complex is reported. Using an MO model of D_{4h} symmetry, the bonding parameters of the first coordination sphere were calculated. The influence of the ligand spin–orbit interaction is considered.

1. Introduction

ESR investigations on transition metal chelates with sulphur- or selenium-containing ligands show some interesting new aspects concerning the bonding properties of the first coordination sphere in these chelates: the degree of covalency of the metal–sulphur, –selenium bonds is found to be very high, the unpaired d-electrons are mainly localized in the ligand rather than on the central metal ion [1–7]. The electronic structure of the coordination sphere is considerably affected by the strong ligand spin–orbit interaction in the heavy donor atoms, which will be reflected by the g-tensor. Thus the g-tensor will be a very sensitive indicator regarding the bonding properties and the symmetry of the first coordination sphere [8].

In this paper, we report the results that have been obtained from single crystal ESR studies of the tetra-*n*-butylammonium salt of copper(II)-bis (1,1-dicyanoethylene-2,2-dithiolate), $[Cu(i\text{-}MNT)_2]$ $(Bu_4N)_2$ (see I), doped in single crystals of the corresponding nickel complex. The bonding parameters of the first coordination sphere are calculated including the ligand spin–orbit coupling in the S-donor atoms. The influence of the organic ligand system on the CuS_4 unit is discussed.



(I)

2. Experimental

Single crystals of $[Ni(i\text{-}MNT)_2]$ $(Bu_4N)_2$ containing approximately 1–2% $[Cu(i\text{-}MNT)_2]$ $(Bu_4N)_2$ were grown by slow evaporation of an acetone solution. The ESR spectra were recorded with a Thomson THN-251 spectrometer (France) in the X-band at room temperature and at 77°K. The magnetic field was calibrated with a ^1H NMR marker; g-values were derived using polycrystalline DPPH as reference.

In order to derive the principal values of the g- and the hyperfine tensors ESR spectra were recorded about every 10° in the planes, defined by the directions of the principal axes of the tensors.

3. ESR spectra

In general, in the single crystal spectra the absorption signals of two $[Cu(i\text{-}MNT)_2]^{2-}$ molecules situated in the unit cell (designated by A and B) are observed. The angular dependence can be described by

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